Effect of Cl/Ni molar ratio on the catalytic conversion of polypropylene into Cu–Ni/C composites and their application in catalyzing "Click" reaction

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ABSTRACT

A one-pot approach to prepare Cu–Ni/C heterogeneous composites by carbonization of polypropylene (PP) using combined catalysts of Ni_2O_3 and CuCl was proposed. TEM, SEM, TGA and Raman measurements were performed to investigate the effects of Cl/Ni molar ratios on the yield and morphology of the resultant carbon materials. The yield of carbon materials in Cu–Ni/C first increased and then decreased as the Cl/Ni molar ratio increased, and the maximum yield was achieved at Cl/Ni molar ratio of 0.125. Longer and thinner carbon nanotubes (CNTs) were obtained at low Cl/Ni ratios while shorter carbon fibers were formed at high Cl/Ni ratios. The effect of Cl/Ni molar ratio on the active sites for the growth of carbon materials and degraded products of PP were investigated by XRD, GC and GC–MS. Interestingly, the resultant Cu–Ni/C showed the catalysis to "Click" reaction. As a result, the initial catalytic substances (Ni_2O_3 and CuCl) could be effectively used twice as catalysts in the carbonization of PP and in the later application of the resultant Cu–Ni/C composites. More importantly, this approach is a new potential method to transform waste polymer materials into valuable metal/carbon heterogeneous composites.

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1. Introduction

Chemical recycling has aroused more and more attention in recent years owing to drastic increase in plastics waste. Mechanical recycling is a preferred recovery route for relatively clean plastics waste, but it is sensitive to unsorted or contaminated plastics waste. Chemical recycling provides a possibility of transforming plastics waste into monomers, fuels, gases and other chemicals using different techniques such as depolymerisation, pyrolysis, catalytic decomposition, solvolysis and gasification, *etc.* Nevertheless, efforts to find a new technically and economically feasible chemical recycling process for the plastics waste have never been given up.

The content of carbon in polyolefin is about 85.7 wt%, thus polyolefin wastes are an affluent resource for the production of carbon materials. Carbon nanotubes (CNTs) has been prepared by catalytic pyrolysis from different types of macromolecules such as polyethylene [1–4], poly(vinyl alcohol) [3], polypropylene (PP) [5,6] and biomass [7]. Recently, a one-step process using autoclave as reactor was used to synthesize CNTs but the high pressure nature of autoclave is not in favor of massive and continuous production [8–10].

Our group has found that the combination of solid acid and nickel catalyst is efficient for high-yielded conversion of virgin or waste PP into CNTs under atmospheric conditions [11–14]. However, the solid acids such as montmorillonite and zeolite must be removed by hydrofluoric acid in order to obtain pure CNTs, which will inevitably increase the operation and cost of the process.

Very recently, our group has found that a synergistic catalysis of a trace of halogen-containing additives with Ni_2O_3 promote the formation of residual char during the combustion of PP [15]. The most of residual char is multi-walled CNTs. The previous work prompted us to raise further questions: how does Cl/Ni molar ratio influence the yield and morphology of the carbon products? If we use metal chloride combining with Ni_2O_3, the catalysts in the resultant carbon products will be easily removed by acid treatment. In addition, considering all the catalysts are metal compounds, it is desirable to regard the resultant carbon products as metal/carbon heterogeneous composites (MCHCs). Then the purification step can be saved and the products with high value can be obtained. MCHCs can be applied to a lot of fields such as catalyzing organic reactions [16–18], biosensors [19], fuel cells [20–22], magnetic materials [23,24], capacitors [25,26], accumulation and storage of hydrogen [27] and wastewater treatment [28–32]. Many kinds of carbon materials (such as CNT, carbon nanofiber and activated carbon) and metals or metal oxides (such as Fe, Co, Cu, Ni, Pt, Pd, SnO_2, TiO_2, and Fe_3O_4) have been used to prepare MCHCs.

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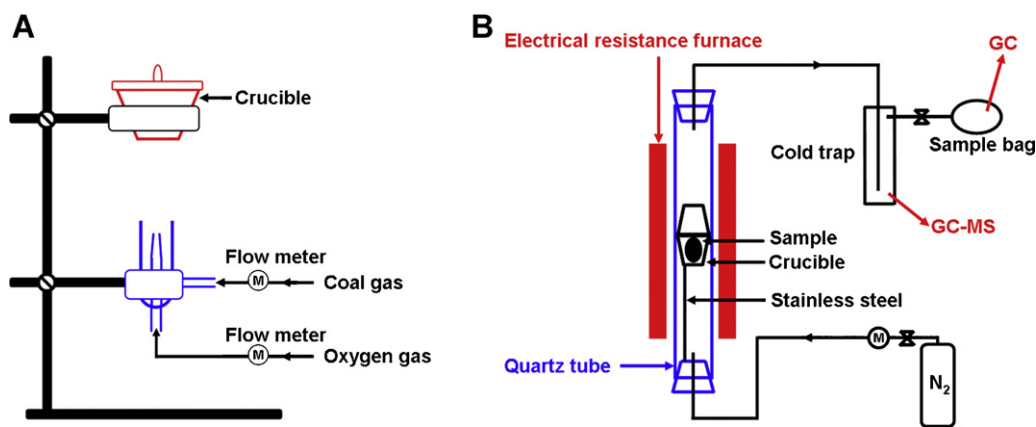
Fig. 1. Schematic diagram of combustion experiment (A) and pyrolysis experiment (B).

Herein, a one-pot approach was established to prepare Cu–Ni/C through the carbonization of PP using combined Ni_2O_3 with CuCl as catalysts. The effects of Cl/Ni molar ratio on the yield of carbon materials, the morphology and phase structure of Cu–Ni/C were studied. Interestingly, the yield and morphology of the resultant MCHCs can be well modulated by altering Cl/Ni molar ratio. The reaction mechanism for this phenomenon was discussed. In addition, the obtained Cu–Ni/C as a heterogeneous catalyst showed good catalytic activity for "Click" reaction, which has been widely applied in bioconjugation, materials science and drug discovery [33].

2. Experimental part

2.1. Materials

Polypropylene (PP) pellet was supplied by Yanan Petrochemical Co., China. Ni_2O_3 (with an average diameter of 250–300 nm, provided by Lingfeng Chemical Company of Shanghai, China), CuCl, NH_4Cl, and $NiCl_2 \cdot 6H_2O$ (from Beijing Yili Fine Chemicals Co., Ltd., China) were of analytical grade quality and used without further purification. Sodiumazide (NaN_3), benzyl bromide (BnBr), phenylacetylene (PhC≡CH) and triethylamine (Et_3N) were purchased from commercial vendors (Sinopharm Chemical Reagents Co., Ltd., China and Alfa Aesar) and used without further purification. Tetrahydrofuran (THF) was freshly distilled over Na/benzophenone ketyl before use.

2.2. Preparation of samples

PP (40.00 g) was mixed with Ni_2O_3 (2.00 g) and a designed amount of chlorinated compound in a Brabender mixer at 100 rpm and 180 °C for 10 min. The resultant samples were designed as PP/MCl/Ni_2O_3-*x*, where MCl and *x* represented the chlorinated compound and the Cl/Ni molar ratio (from 0.01 to 1), respectively. For comparison, PP/*y*CuCl was prepared, where *y* meant the weight percentage of CuCl. PP/Ni_2O_3 was also prepared with Ni_2O_3 content of 5 wt%.

2.3. Preparation of MCHCs

MCHCs were prepared by combustion experiment as shown in Fig. 1(A) and designated as M/C-*x*, where M and *x* represented the metal elements and the Cl/Ni molar ratio, respectively. The temperature of flame was controlled by adjusting the flows of coal gas and oxygen gas. Briefly, a piece of sample (~5.0 g) was placed into a crucible, which was heated at 700 °C until the flame from the crucible

upper brim went out. The obtained M/C-*x* was cooled to room temperature and weighed. The yield of carbon materials (g/100 g PP) in the obtained MCHCs was calculated by the amount of the residue after subtracting the amount of the residual catalysts divided by the amount of PP in the sample.

The degraded products of PP are the carbon feedstock for the formation of carbon materials. The Cl/Ni molar ratio may affect the degraded products of PP. To deeply study the effects of Cl/Ni molar ratios on the degraded products of PP, pyrolysis experiment was conducted in a fixed bed reactor as a model experiment (shown in Fig. 1(B)). The quartz tube with a crucible in the middle was vertically mounted in an electrical resistance furnace and heated to 700 °C in N_2 atmosphere (N_2 was used to blow off the air in the tube before pyrolysis and the degraded products after pyrolysis). Subsequently, a sample (~2.5 g) was put into the crucible and pyrolyzed at 700 °C. The liquid pyrolyzed products were collected using a cold trap and the gas products were collected using a sample bag.

2.4. Cu–Ni/C catalyzing "Click" reaction

The "Click" reaction catalyzed by the obtained Cu–Ni/C-0.5 was shown in Scheme 1. Benzyl azide (BnN_3) from $NaN3$ and BnBr was synthesized as described earlier [34]. The obtained Cu–Ni/C-0.5 was crushed and dried under vacuum at 120 °C overnight. The dried Cu–Ni/C-0.5 was stirred in THF and dispersed by ultrasonic treatment for 10 min to prepare Cu–Ni/C-0.5 suspension. The triazole was synthesized according to the literature method [35] with some modifications. Et_3N (5 mmol), BnN_3 (5 mmol) and PhC≡CH (5 mmol) were added into the obtained Cu–Ni/C-0.5 suspension under argon and stirred at 65 °C for 36 h. After the reaction, the mixture was filtered to remove Cu–Ni/C-0.5. The volatiles were removed under vacuum and the triazole was isolated as a white solid (1.14 g, 97%, 1.18 g theoretical yield), which was confirmed by ^{1}H NMR.

2.5. Characterization

The morphology of the Cu–Ni/C composites was observed by means of field-emission scanning electron microscope (FE-SEM, XL30ESEM-FEG) and field-emission transmission electron microscope (FE-TEM, JEM-2010 operating at 200 kV). The phase structure of the Cu–Ni/C composites were analyzed by X-ray powder diffraction (XRD) using a D8 advance X-ray diffractometer with Cu Kα radiation operating at 40 kV and 200 mA. The thermal stability of the Cu–Ni/C composites was measured by thermal gravimetric analysis (TGA) under air flow from room temperature to 700 °C

1-Benzyl-4-phenyl-1*H*-1,2,3-triazole
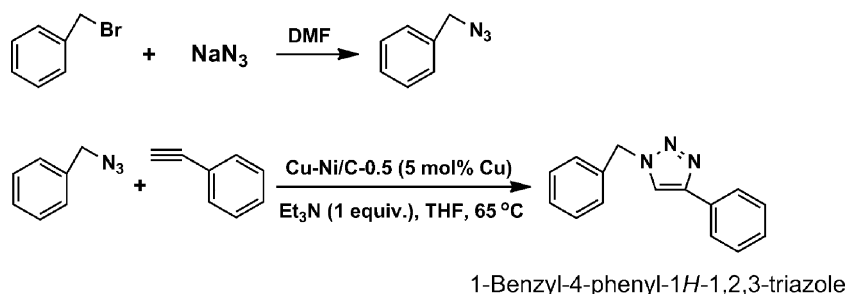
Scheme 1. "Click" reaction catalyzed by the obtained Cu–Ni/C-0.5.

at a heating rate of 10 °C/min using TA Instruments SDT Q600. The vibrational properties of the Cu–Ni/C composites were characterized by a Renishaw 2000 model confocal microscopy Raman spectrometer using the 514.5 nm diode laser. The confirmation and purity of "Click" reaction product were characterized by ^{1}H NMR spectra using a Varian Unity 400 MHz spectrometer at 25 °C in $CDCl_3$.

The liquid fraction of pyrolyzed products during the formation of Cu–Ni/C composites was weighed and then analyzed by gas chromatography–mass spectrometry (GC–MS, AGILENT 5975MSD). The volume of gas products was determined by the displacement of water. The organic gases were analyzed by a GC (Kechuang, GC 9800) equipped with a FID, using a KB–Al_2O_3/Na_2SO_4 column (50 m × 0.53 mm ID). The permanent gases (H_2, N_2, CO, O_2, CH_4 and CO_2) were analyzed by a GC (Kechuang, GC 9800) equipped with a TCD, using a packed TDX-01 (1 m) and a zeolite 5A column (1.5 m).

3. Results and discussion

3.1. Effect of Cl/Ni molar ratio on the yield of carbon materials in MCHCs

Fig. 2 presents the effects of Cl/Ni molar ratios on the yield of carbon materials in MCHCs. Three kinds of chlorinated compounds (CuCl, NH_4Cl and $NiCl_2$·6H_2O) were added into PP/Ni_2O_3 mixture, respectively. In the case of PP/Ni_2O_3, the yield of carbon materials was as low as 4.5 wt%. Interestingly, the variation of carbon materials yield after adding different chlorinated compounds showed similar trends, that is, the yield of carbon materials increased at first and then decreased with the increase of Cl/Ni molar ratio.
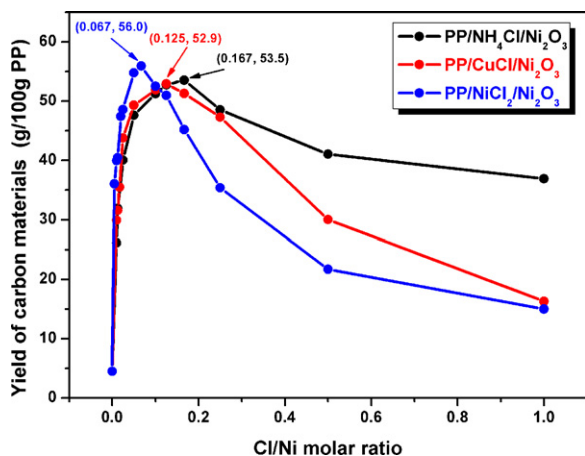

Fig. 2. Effect of Cl/Ni molar ratios on the yield of carbon materials in MCHCs at 700 °C. Each measurement was repeated on four different samples for reproducibility purpose with standard error less than 1.6%.

For example, after adding a trace amount of CuCl (Cl/Ni = 0.01) to PP/Ni_2O_3 mixture, the yield of carbon materials in Cu–Ni/C composites increased rapidly to 29.9 wt% and reached the maximum value of 52.9 wt% at a Cl/Ni molar ratio of 0.125. The yield of carbon materials reached a maximum at a Cl/Ni molar ratio of 0.167 and 0.067 for PP/NH_4Cl/Ni_2O_3 and PP/$NiCl_2$/Ni_2O_3, respectively. The above results suggest that Cl/Ni molar ratio is the most important factor for the yield of carbon materials, regardless of what chlorinated compounds are used. Thus, M–Ni/C composites with various amounts of carbon materials can be prepared by adjusting the Cl/Ni molar ratio.

3.2. Effect of Cl/Ni molar ratio on the morphology of Cu–Ni/C

To identify whether Cl/Ni molar ratio has any effects on the morphology of the resultant carbon materials, SEM observation for the carbon materials was performed (Fig. 3). Carbon materials obtained at lower Cl/Ni molar ratios (≤0.125) were mainly in the form of long fibers. The mean diameter increased from 66 to 88 nm and the average length decreased from 6.5 to 2.7 μm as Cl/Ni molar ratio increased from 0.0125 to 0.125. When the Cl/Ni molar ratio further increased to 0.25 and 0.5, the obtained carbon materials were most of short fibers.

Fig. 4 shows the TEM images of Cu–Ni/C composites from different Cl/Ni molar ratios obtained at 700 °C. At Cl/Ni molar ratio lower than 0.125, the majority of filamentous carbon had a tubular form with central hollow inside, indicating that the produced carbon materials were CNTs. The shape of the CNTs was relatively straight and long. At higher Cl/Ni molar ratios, more short and winding carbon nanofibers were produced and the surfaces appeared to be rugged. TEM and SEM observations together indicated that the yield and morphology of carbon materials in M–Ni/C composites could be modulated by adjusting Cl/Ni molar ratios. Moreover, the metal in M–Ni/C composites can be modified by using different metal chloride compounds.

TGA was used to measure the thermal stability of Cu–Ni/C composites. As shown in Fig. 5, the oxidation peak position shifted towards lower temperature with the increase of Cl/Ni molar ratio, indicating the formation of more amorphous carbon, poorly graphitized CNTs or both at higher Cl/Ni molar ratios, which is agreement with the results of SEM and TEM observation.

Fig. 6 displays the Raman spectra of Cu–Ni/C composites from different Cl/Ni molar ratios at 700 °C. The peak at about 1581 cm^{-1} (G band) corresponds to an E_{2g} mode of hexagonal graphite and is related to the vibration of sp^2-bonded carbon atoms in a graphite layer, and the D band at about 1347 cm^{-1} is associated with vibration of carbon atoms with dangling bonds in the plane terminations of disordered graphite or glassy carbons. The intensity of the D and G bands provides information about the crystallinity of carbon materials. With the increase of Cl/Ni molar ratio from 0.0125 to 0.5, the I_G/I_D ratio of carbon materials from Cu–Ni/C
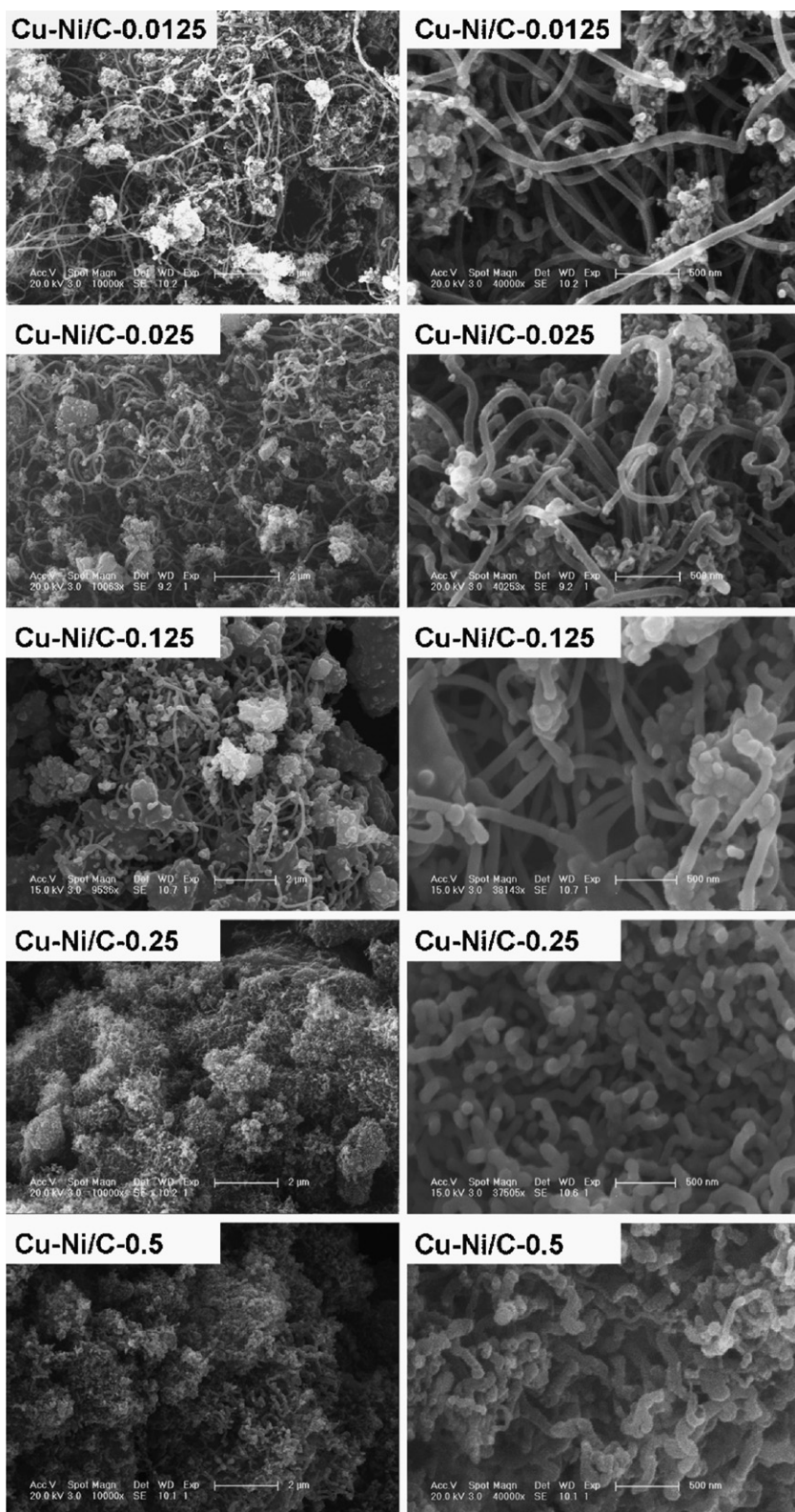
Fig. 3. SEM images of Cu–Ni/C composites from different Cl/Ni molar ratios at 700 °C.

composites decreased from 0.69 to 0.59. The result indicates that carbon materials in Cu–Ni/C composites from lower Cl/Ni molar ratios have relatively lower defects inside the graphite sheet or less content of amorphous carbon than those from higher Cl/Ni molar ratios. This result is consistent with those of SEM, TEM and TGA.

3.3. Mechanism about the effect of Cl/Ni molar ratio on the yield and morphology of Cu–Ni/C

Based on the previous reports [36–46], the growth of CNTs from degraded products of PP using combined catalysts of Ni_2O_3 and CuCl could be deemed as "tip growth" model through
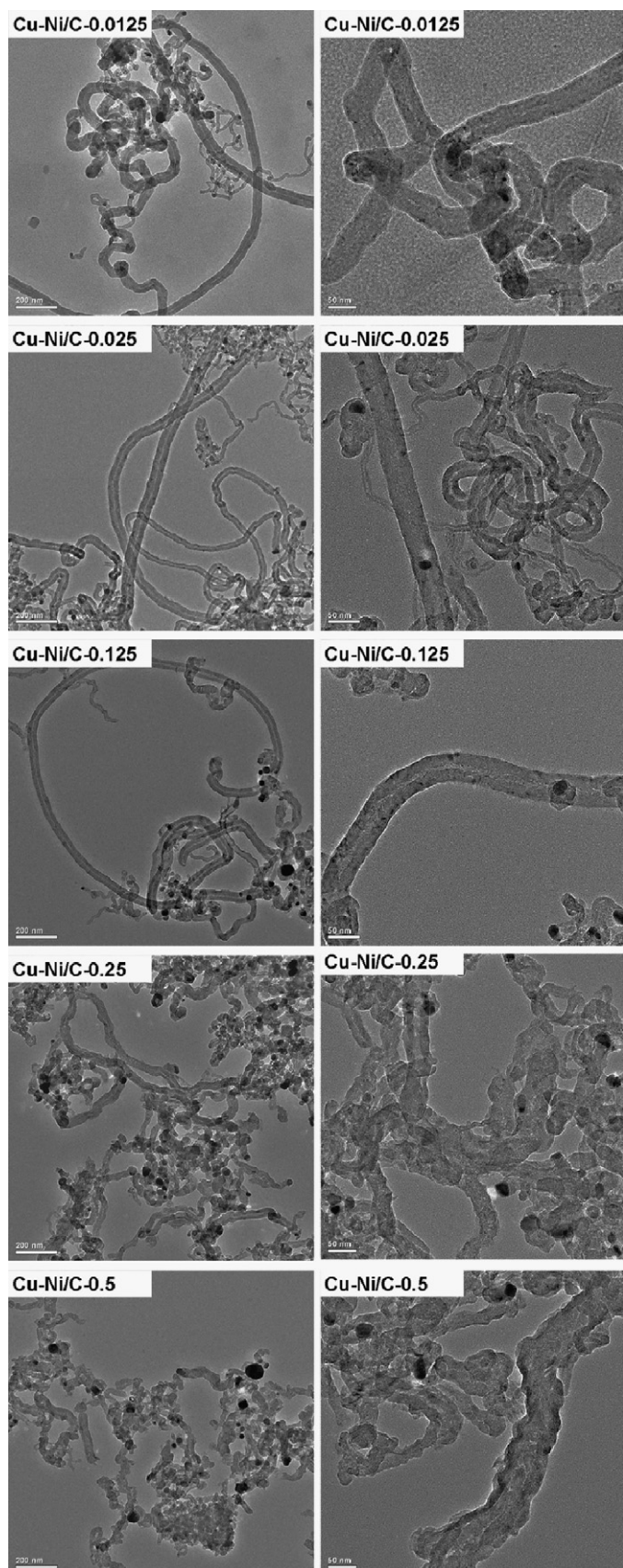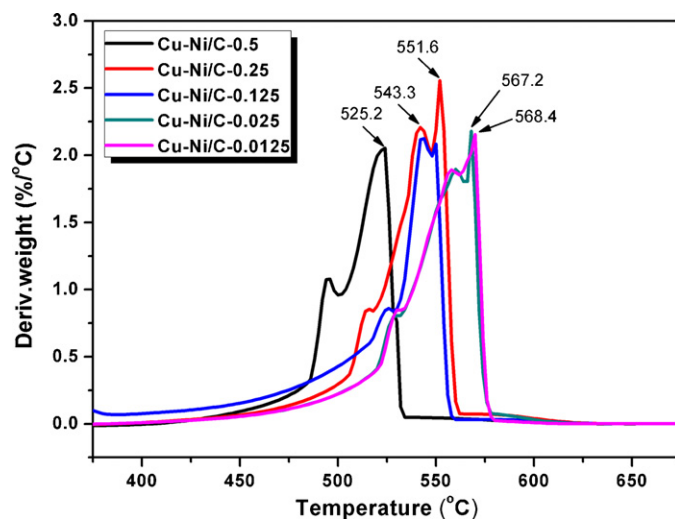
Fig. 5. DTG curves of Cu–Ni/C composites from different Cl/Ni molar ratios at 700 °C under air flow.

a dissociation–diffusion–precipitation process. Briefly, hydrocarbons generated from the degradation of PP are first pyrolyzed into "free carbons", which dissolve in and diffuse through the bulk of Ni catalyst reduced from Ni_2O_3 driven by a temperature or concentration gradient, and then precipitate in the form of graphite at the surface of Ni catalyst. The "bud" of CNT is finally formed and begins to grow by continuous formation of graphite until Ni catalyst is totally poisoned or the reaction is over.

In this work, the solubility of carbon in Cu is very low [47], and the content of Cu is also lower than that of Ni for low Cl/Ni molar ratios. Thus the catalytic activity of Cu can be neglected under the conditions. The carbon feedstock and catalyst are essential for the formation of CNTs, so we discussed the effect of Cl/Ni molar ratio on the nickel catalyst and degraded products of PP to clarify the reason for the variation of yield and morphology of CNTs.

3.3.1. Effects of Cl/Ni molar ratio on the reduction from Ni_2O_3 to Ni

Fig. 7 shows XRD patterns of Cu–Ni/C-x composites and PP/Ni_2O_3 mixture. Compared to the XRD pattern of PP/Ni_2O_3 mixture, the diffraction peaks of both graphite and metallic nickel appeared in the obtained Cu–Ni/C while the diffraction peaks of PP
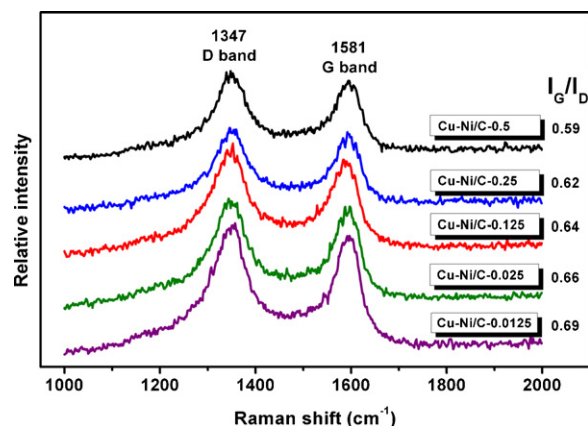

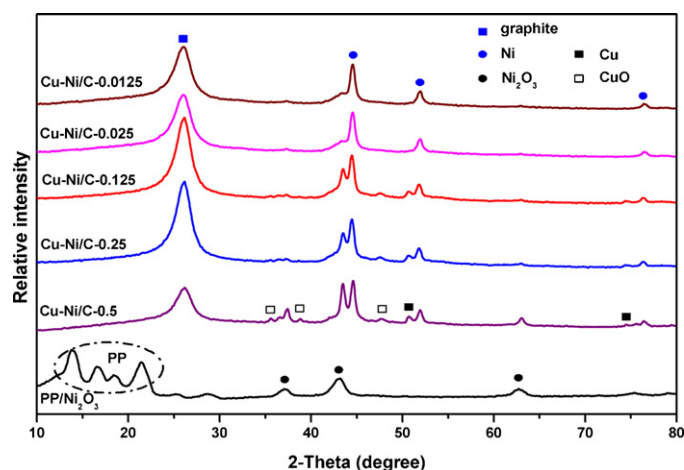**Fig. 4.** TEM images of Cu–Ni/C composites from different Cl/Ni molar ratios at 700 °C.

Fig. 6. Raman spectra of Cu–Ni/C composites from different Cl/Ni molar ratios at 700 °C.

Fig. 7. XRD patterns of Cu–Ni/C-*x* composites and PP/Ni$_2$O$_3$ mixture.
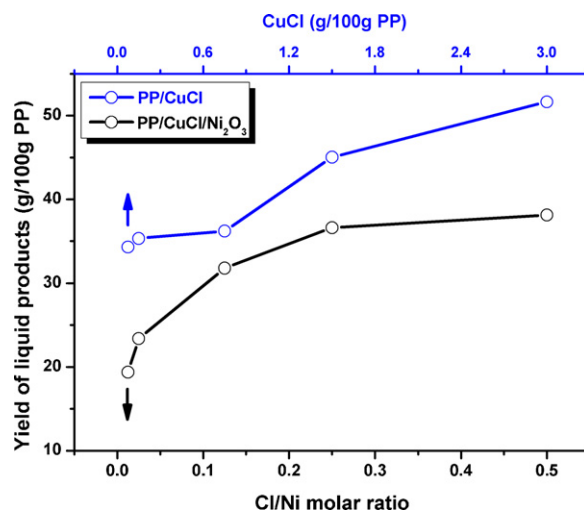

Fig. 8. Effect of the content of CuCl or Cl/Ni molar ratio on the yield of liquid products from PP mixtures pyrolyzed at 700 °C. Each measurement was repeated at least three different samples and the averaged values was reported with standard error less than 1.5%.

disappeared. The diffraction peaks of Cu and CuO were very weak even for the Cu–Ni/C-0.5, possibly because Cu species are mainly in amorphous state or the content of Cu species is below the detection limit. No diffraction peaks of other Cu species (such as CuCl, Cu$_2$O) were detected in the obtained Cu–Ni/C. Ni$_2$O$_3$ could be *in situ* reduced to Ni by hydrogen gas or hydrocarbons from the degradation of PP. However, the diffraction peaks of Ni$_2$O$_3$ still existed at

higher Cl/Ni molar ratios. That is to say, a part of Ni$_2$O$_3$ remained, especially in Cu–Ni/C-0.5. The incomplete reduction of Ni$_2$O$_3$ to Ni is partially responsible for the variation of the yield of CNTs in Cu–Ni/C, which will be discussed in the latter.
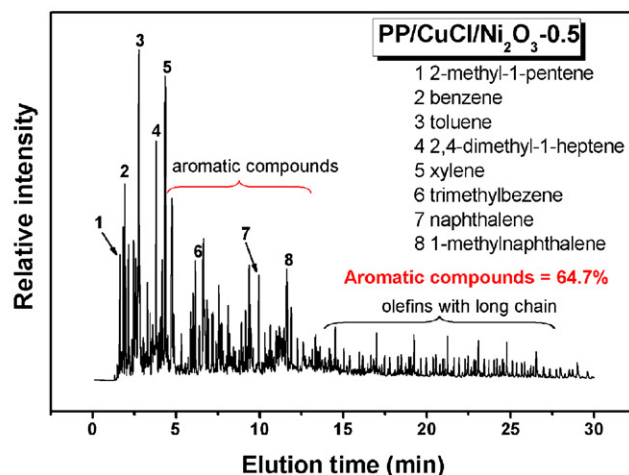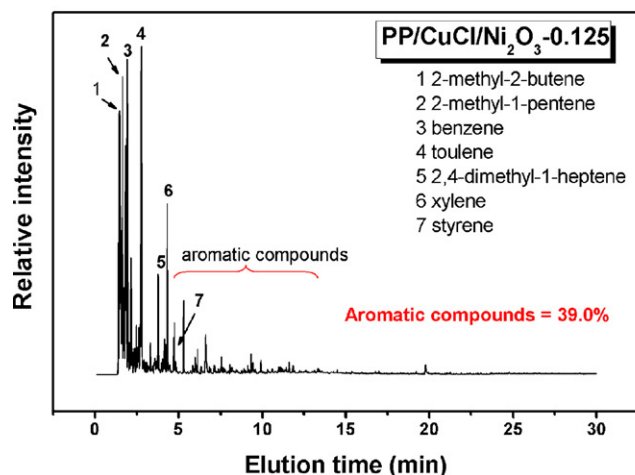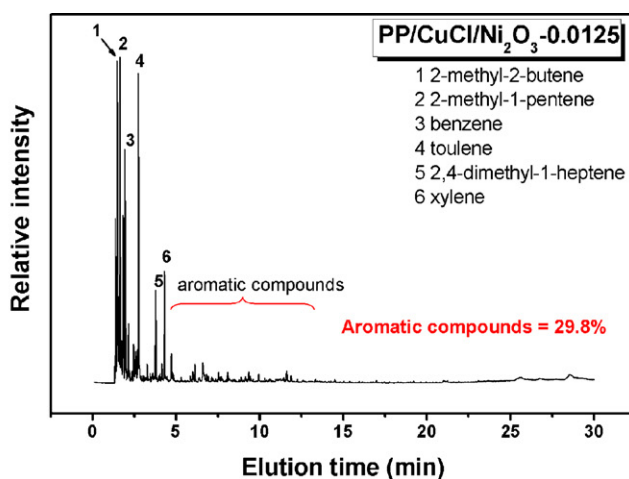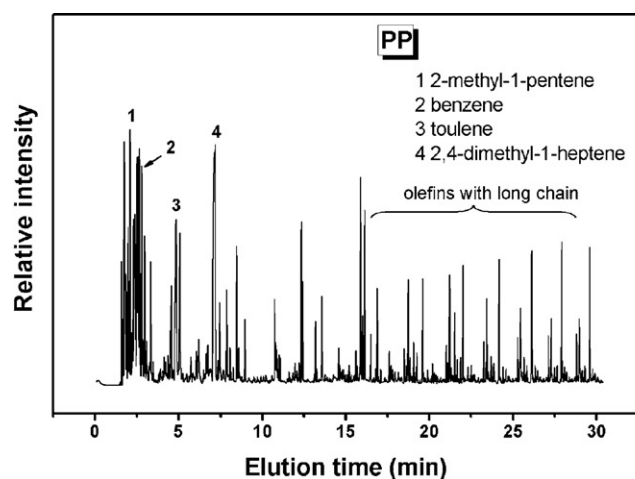

Fig. 9. GC–MS profiles for the liquid fraction of degraded products from PP and PP/CuCl/Ni$_2$O$_3$-*x* mixtures pyrolyzed at 700 °C.

Fig. 10. The composition of gas products from PP and PP/CuCl/Ni$_2$O$_3$-x mixtures pyrolyzed at 700 °C.

Fig. 11. Possible formation process of M–Ni/C composites through catalytic conversion of PP using combined catalysts of Ni$_2$O$_3$ and chlorinated compound.
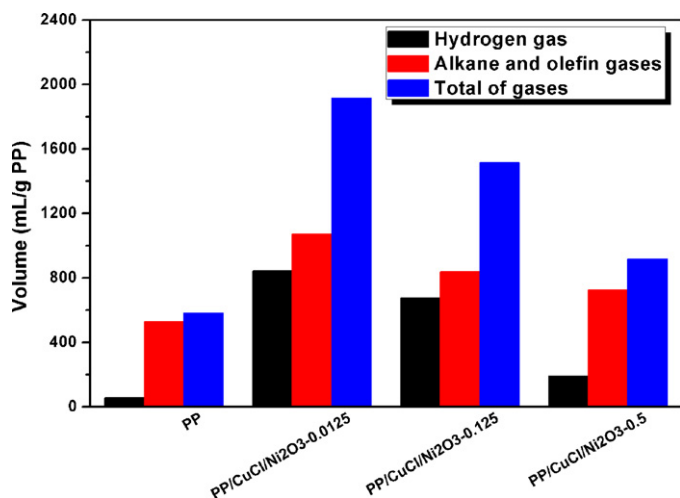
3.3.2. Effects of Cl/Ni molar ratio on the liquid products

The degraded products of PP are the carbon feedstocks for the growth of CNTs. The chlorine content may affect the degraded products and then determine the formation of CNTs. Fig. 8 shows the yield of liquid products from PP mixtures with different CuCl contents or Cl/Ni molar ratios. The yield of liquid products from both the mixtures went up with increasing CuCl since CuCl could promote dehydrogenation and aromatization during the degradation of PP [15]. Fig. 9 shows the GC–MS profiles for the liquid fraction of degraded products from PP and PP/CuCl/Ni$_2$O$_3$ mixtures pyrolyzed at 700 °C. The distribution of degraded products from PP was broad, and olefins with long chain emerged at higher elution time accounted for a large percentage. When the Cl/Ni molar ratio was low, the olefins with long chain almost disappeared while they appeared with the increase of Cl/Ni molar ratio to 0.5. The same phenomenon was also observed for the aromatic compounds. Light hydrocarbons are considered as the carbon feedstock for the growth of CNTs. Combining with the results shown in Fig. 2, the aromatic compounds were favorable to enhance the yield of CNTs because olefins with long chains can not easily form CNTs over Ni catalyst. Dai [48] has reported that a small concentration of benzene led to an appreciable increase in the yield of long CNTs in the methane chemical vapor deposition (CVD) approach, but further increasing the concentration of benzene resulted in exceedingly low yield of CNTs. The possible reason was that benzene was highly reactive compared to methane, but high concentration of benzene underwent extensive pyrolysis, in which the formation of amorphous char on the surface of Ni particles caused severe catalyst poisoning, as a result, the growth of CNTs was blocked.

The catalyst deactivation is a common phenomenon in the decomposition of gaseous hydrocarbons to produce hydrogen gas and carbon, where Ni, Fe, Co and Pd show drop in their catalytic activity due to deposition of carbon [49,50]. Similarly in this work, as Cl/Ni molar ratio increased, extensive self-pyrolysis from more amount of heavy hydrocarbon products may occur on the surfaces of Ni and Ni$_2$O$_3$, which is not in favor of the reduction of Ni$_2$O$_3$, leads to the Ni catalyst more susceptible to poisoning effect and limits the growth of CNTs. Finally, shorter and coarser CNTs were formed in Cu–Ni/C composites at high Cl/Ni molar ratios.

3.3.3. Effect of Cl/Ni molar ratio on the gas products

Fig. 10 displays the composition of gas products from PP and PP/CuCl/Ni$_2$O$_3$-x mixtures pyrolyzed at 700 °C. The gases from these samples mainly consisted of hydrogen, methane, ethane,

ethylene, propane, propylene and butane. Light hydrocarbons are considered as the carbon feedstocks to form CNTs [13]. The yield of light hydrocarbons from PP/CuCl/Ni$_2$O$_3$-0.0125 was the highest. However, the highest yield of carbon materials was obtained at the Cl/Ni molar ratio of 0.125, which indicated that other compounds are also contributed to the growth of CNTs. Compared to PP, more hydrogen was produced after the addition of CuCl and Ni$_2$O$_3$. The hydrogen yield of PP/CuCl/Ni$_2$O$_3$-0.0125 was 4.4 times than that of PP/CuCl/Ni$_2$O$_3$-0.5. This may be due to the promotion of dehydrogenation by chlorine radical, but the presence of more chlorine radical also improves the aromatization of degraded products. Thus, with the increase of Cl/Ni molar ratio, the content of hydrogen decreased and the amount of aromatic compounds increased, which is evidenced by GC–MS results. It can be inferred that both light hydrocarbons and aromatics are the carbon feedstocks to produce CNTs. Additionally, from SEM and TEM observations, we can also infer that straight and regular CNTs tend to be produced by light hydrocarbons and aromatics yield more short carbon fibers. Besides, it cannot be excluded that the growth of CNTs is promoted by hydrogen gas etching amorphous char deposited on the surfaces of catalyst and CNTs [51,52].

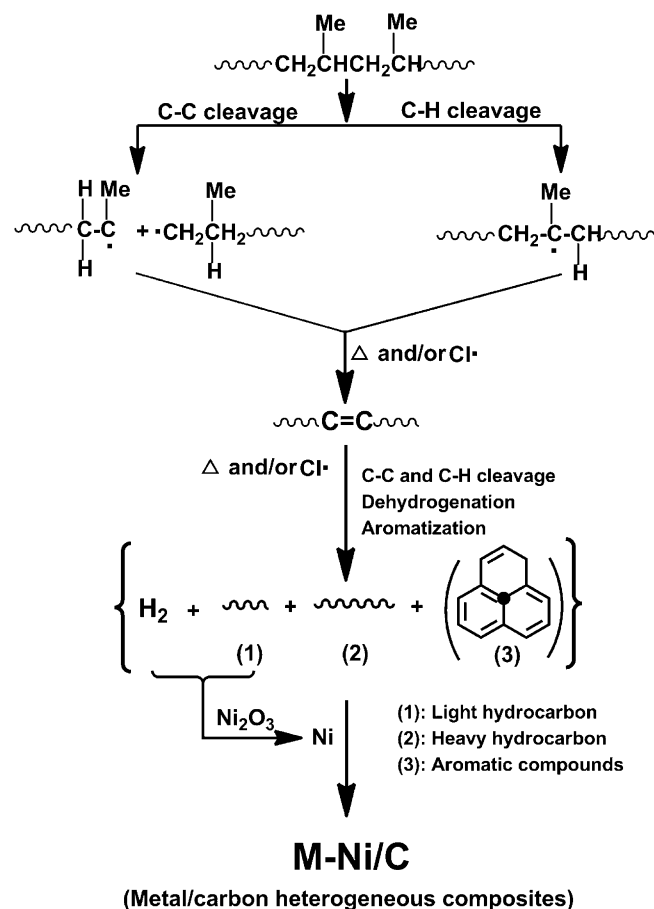Based on the above results and the previous report [15], a possible formation process of M–Ni/C composites through catalytic conversion of PP using combined catalysts of Ni$_2$O$_3$ and chlorinated compound is shown in Fig. 11. PP macroradicals are generated by cleavage of C—C or C—H bond on PP backbone. Chlorine radicals can promote the dehydrogenation and aromatization reaction of macroradical fragments. With further C—C and C—H cleavage and dehydrogenation, a mass of light hydrocarbons are produced. Light hydrocarbons and aromatics are the carbon feedstocks to form
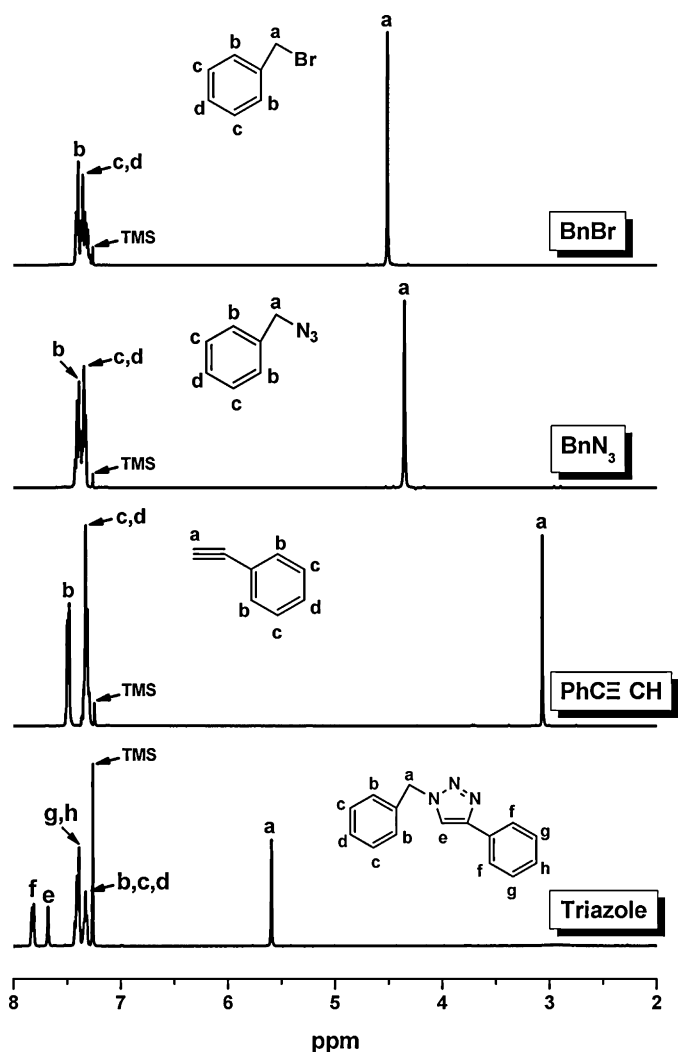
Fig. 12. ^{1}H NMR spectra of BnBr, BnN$_3$, PhC≡CH and the obtained triazole.

CNTs. When the Cl/Ni molar ratio is low, dehydrogenation prevails over aromatization, thus a low quantity of aromatic compounds are formed. The relatively low quantity of aromatic compounds together with high quantity of hydrogen and light hydrocarbon promote the formation of more CNTs. However, when the Cl/Ni molar ratio increases, more aromatization reaction occurs, leading to high content of aromatic compounds, which is responsible for the formation of more carbon nanofiber and little CNTs. Therefore, the content of CuCl affects the quantity and composition of both the gas and liquid degraded products from PP. As a result, the Cl/Ni molar ratio determines the yield, morphology and phase structure of carbon materials in the resultant Cu–Ni/C composites.

4. Cu–Ni/C-0.5 as a heterogeneous catalyst for "Click" reaction

Fig. 12 displays the ^{1}H NMR spectra of BnBr, BnN$_3$, PhC≡CH and the obtained triazole. The singlet signal at 4.49 ppm assignable to CH$_2$ in BnBr up-field shifted to 4.33 ppm, confirming the successful synthesis of BnN$_3$. After Cu–Ni/C-0.5 (5 mol% Cu) catalyzed the reaction of BnN$_3$ with PhC≡CH at 65 °C for 36 h, the peak at 4.33 ppm for CH$_2$ in BnN$_3$ and the one at 3.07 ppm for CH of acetylene in PhC≡CH totally disappeared, meanwhile the peak at 5.59 ppm for the CH$_2$ from the resultant triazole appeared, demonstrating that

the obtained Cu–Ni/C-0.5 can be used to catalyze "Click" reaction with high yield (97%).

On one hand, it should be noted that the reaction time of "Click" reaction in this study is longer than that in the previous report [17,35], possibly due to amorphous carbon covering the Cu particles in the obtained Cu–Ni/C-0.5, leading to insufficient catalysis for this reaction. Studies on how to further adjust the morphology of metal/carbon heterogeneous composites, promote the catalytic efficiency and finally explore proper reaction conditions for a designed application will be conducted in the following reports.

On the other hand, since the obtained Cu–Ni/C also contains a part of Ni(0), which is regarded as catalyzing substance for other chemical reactions such as Suzuki–Miyaura reaction [53], it is speculated that the resultant Cu–Ni/C could also catalyze other organic chemical reactions, and further research work is under way.

5. Conclusions

A one-pot approach to largely produce Cu–Ni/C composites by synergistic carbonization of PP using combined catalysts of Ni$_2$O$_3$ and CuCl was demonstrated. As Cl/Ni molar ratio increased, the yield of carbon materials first increased and then decreased. The maximum yield was achieved at the optimal Cl/Ni molar ratio of 0.125. Meanwhile, lower Cl/Ni molar ratios yielded Cu–Ni/C with longer and thinner CNTs. The Cl/Ni molar ratio affected the reduction from Ni$_2$O$_3$ to Ni and the composition of both gas and liquid degraded products, which finally determined the yield of carbon materials, the morphology and phase structure of the resultant Cu–Ni/C composites. Therefore, it is easy to produce Cu–Ni/C with different compositions and various microstructures by adjusting Cl/Ni molar ratio. The resultant Cu–Ni/C can catalyze "Click" reaction with the yield up to 97%, indicating the obtained Cu–Ni/C have the potential application in the organic chemistry. It should be mentioned that the initial catalytic substances (Ni$_2$O$_3$ and CuCl) could be effectively used as catalysts twice in the carbonization of PP and in the later application of the resultant Cu–Ni/C composites. More importantly, this approach is a new potential method to transform waste polymer materials into valuable metal/carbon heterogeneous composites. This work also offers the possibility for the large fabrication of other metal/carbon heterogeneous composites. Studies on how to further adjust the composition and morphology of metal/carbon heterogeneous composites to meet some applications will be conducted in the following reports.

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